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Template-Synthesized Polyacetylene Fibrils
Show Enhanced Supermolecular Order

by

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TEMPLATE-SYNTHESIZED POLYACETYLENE FIBRILS SHOW
ENHANCED SUPERMOLECULAR ORDER

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ABSTRACT

We have recently described a template method for synthesizing nanoscopic conductive polymer fibrils. In this method, the pores in a nanoporous host membrane are used as templates for the nascent conductive polymer. We have shown that such template-synthesized fibrils show significantly higher conductivities than bulk films of the analogous polymer. We suggested that this enhanced conductivity results from preferential orientation of the polymer chain parallel to the fibril axis. This paper provides the first experimental proof for such enhanced supermolecular order in template-synthesized conductive polymer fibrils. We describe (for the first time) the template synthesis of nanoscopic polyacetylene fibrils. We demonstrate (using a polarized infrared absorption experiment) that the polymer chains in these fibrils are preferentially oriented parallel to the fibril axis. This is the first example of preferential chain orientation in a conductive polymer without post polymerization processing or synthesis in a liquid crystal solution.



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We have recently described the synthesis of nanoscopic fibrils of heterocyclic polymers (1). These fibrils were synthesized via a template method, in which the pores in a nanoporous membrane act as templates for the nascent polymer. Such fibrils show electronic conductivities (along the fibril axis) which are substantially higher than conductivities of bulk films of the analogous polymer (1). We suggested that this enhanced conductivity resulted from preferential orientation of the polymer chains parallel to the fibril axis (1); however, we had no experimental data to support this contention.

This correspondence provides experimental proof for such enhanced supermolecular order in template-synthesized conductive polymer fibrils. We describe (for the first time) the template synthesis of nanoscopic polyacetylene fibrils. We then present results of a polarized infrared absorption experiment which prove that the polyacetylene chains in these fibrils are preferentially oriented parallel to the fibril axis. Finally, we show that these fibrils have higher electronic conductivities than polyacetylene film synthesized under identical conditions. These studies provide the first example of preferential chain orientation in a conductive polymer without post polymerization processing or synthesis in a liquid crystal solution (2).

Fibrils were synthesized by polymerizing acetylene within the pores (dia = 200 nm) of an Anopore (3) filtration membrane. The polymerization catalyst was $\text{Ti}(\text{OBu})_4/\text{AlEt}_3$ (4). The Anopore membrane and catalyst solution were added to the polymerization

vessel (a septum-sealed glass tube). The catalyst solution was impregnated into the pores of the host by evacuating the vessel, heating to 70° C, and then back filling with Ar. The excess catalyst was removed with a syringe. The vessel was then evacuated again and acetylene gas (5) was introduced.

Polymerization was allowed to proceed for 2 hours, at 0° C (6). The membrane was then washed in sequence with degassed toluene, 5% HCl in methanol, and pure methanol, and then dried in vacuo.

Figure 1 shows a scanning electron micrograph of the polyacetylene fibrils. This micrograph was obtained by dissolving the Anopore membrane (3) and then collecting the fibrils by filtration. The fibrils show good monodispersity of both length and diameter; this is a characteristic feature of the template method.

The polarized infrared absorption (PIRA) experiment (7) was conducted on the Anopore-polyacetylene composite membrane. (Leaving the fibrils embedded in the Anopore membrane insured that all of the fibrils were oriented in the same direction in space.) The composite membrane was positioned at an angle of 45° (8) with respect to the incident beam of the spectrometer (9). A gold wire grid polarizer was used to control the angle of polarization of the incident beam. The absorbance of the composite membrane by radiation polarized perpendicular and parallel (8) to the fibril axes was measured (Figure 2).

Polyacetylene was chosen for these studies because analogous PIRA investigations have been conducted on stretched

polyacetylene film (2). Stretching causes preferential orientation of the polyacetylene chains parallel to the stretch axis and the effects of this preferential orientation on the PIRA spectra have been well documented (2). These investigations serve as references points for the data obtained in this study.

PIRA spectra for the C-H stretching mode in the polyacetylene fibrils are shown in Figure 2 (10). In analogy to the stretch-oriented material (2), the fibrils preferentially absorb light polarized parallel to the fibril axis. The dichroic ratio, R (7), can be obtained from the PIRA spectra; ($R = A_{||}/A_{\perp}$, where $A_{||}$ and A_{\perp} are the integrated absorption intensities for light polarized parallel (8) and perpendicular, respectively, to the fibril axes).

An R value of 1.46 was obtained from the spectra in Figure 2, indicating that the polymer chains in these fibrils are preferentially oriented (see below). It is important to point out that virgin Anopore membrane shows $R=1.0$ (no orientation). Furthermore, when the composite membrane is oriented at an angle of 90° relative to incident beam, $R=1.0$ is also obtained; this is expected because this 90° orientation insures that the vectors for both polarizations are normal to the fibril axes. These studies serve as controls for the data in Figure 2.

A quantitative picture of the supermolecular structure in these fibrils can be obtained by calculating the average orientation angle (θ) between the polymer chains and the fibril axis (7). This calculation requires a value for R and for the

angle (α) between the transition moment of the vibration and the axis of the polymer chain (7). Investigations of stretch-oriented polyacetylene (2) have shown that $\alpha=48^\circ$ for the C-H stretching mode. The orientation angle can vary from $\theta=90^\circ$ (polymer chains oriented perpendicular to the fibril axis) to $\theta=0^\circ$ (chains oriented parallel to the axis). A θ value of 22.5° is obtained for the polyacetylene fibrils, indicating a high degree of parallel orientation.

If the polymer chains are, indeed, oriented parallel to the fibril axis, then conductivity along this axis should be enhanced (1,2). Conductivity along the fibril axis was measured using the method described in (1); p-doped samples were investigated (11). A conductivity of 1425 S cm^{-1} was obtained. Conventional polyacetylene film, synthesized and doped under identical conditions, showed a conductivity of 325 S cm^{-1} . Thus, the parallel polymer chain orientation does, indeed, yield enhanced electronic conductivity along the fibril axis.

We have shown that template-synthesis yields enhanced supermolecular order and higher electronic conductivities in conductive polymers. We are currently developing a mechanistic model for this enhanced order. We are also exploring the extent to which other types of polymers can be ordered via the template method. Template synthesis may prove to be a general procedure for obtaining highly ordered nanoscopic polymeric fibrils.

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5. Acetylene (99.6 %, Scott) was purified by passage through concentrated H_2SO_4 and a column of activated alumina.
6. As was observed previously (1), template synthesis yielded conductive polymer fibrils running through the membrane and thin polymer films covering both faces of the membrane. These surface layers were peeled from the membrane faces.
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8. The ideal geometry for these measurements would be to impinge the light onto the edge of the membrane so that the parallel polarization would be truly parallel to the axes of the fibrils. This is not possible because the membranes are only 55 μm -thick. For this reason the 45° geometry was adopted. In this geometry, the polarization vector for the "parallel" component is coplaner with the axis of the fibril but intersects the fibril at an angle of 45°. Thus, only a component of the "parallel" polarization is truly parallel to the fibril axis. The effects of this geometrical arrangement were accounted for (7) in the determination of the orientation angle (θ).
9. An IBM IR/30 FTIR spectrometer was used.
10. Undoped polyacetylene shows only a few distinct IR bands (2). These other bands are buried beneath the Anopore absorption.
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Figure 1. Scanning electron micrograph of template-synthesized polyacetylene fibrils.

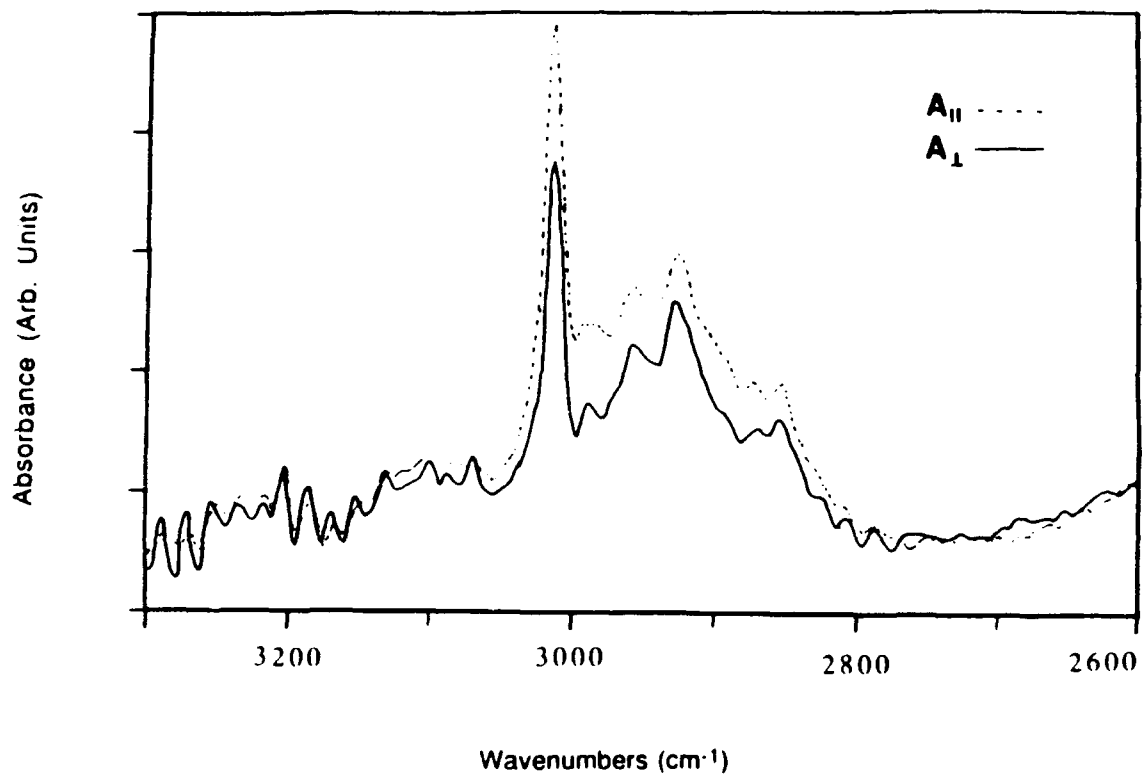


Figure 2 - Polarized infrared absorption spectra (in the C-H stretching region) for an Anopore membrane/polyacetylene fibril sample. $A_{||}$ and A_{\perp} are absorbances parallel (\parallel) and perpendicular to the fibril axis.